

A thermostated coupled apparatus for the simultaneous determination of adsorption isotherms and differential enthalpies of adsorption at high pressure and high temperature

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Abstract In order to assess and improve the quality of high pressure and temperature adsorption isotherms and differential enthalpies of adsorption on microporous and mesoporous materials, a specific thermostated device comprising a differential heat flow calorimeter coupled with a home-built manometric system has been built. The differential heat flow calorimeter is a Tian Calvet Setaram C80 model which can be operated isothermally, the manometric system is a stainless steel homemade apparatus. The thermostated coupled apparatus allows measurements for pressure up to 2.5 MPa and temperature from 303 to 423 K. Reliability and reproducibility were established by measuring adsorption isotherms on a benchmark sorbent (Filtrisorb F400). A detailed experimental study of the adsorption of pure carbon dioxide and methane has been made on activated carbons (Filtrisorb F400 and EcoSorb); a new procedure for determining the differential enthalpies of adsorption based on the stepwise method is also proposed. The error in the determination of the amount adsorbed is about 3.6%, and the error in the determination of the differential enthalpies of adsorption is 4%.

Keywords Adsorption · Calorimeter · Microporous materials · Activated carbons · High pressure · High temperature · Carbon dioxide · Methane

Introduction

Adsorption isotherms and differential enthalpies of adsorption at high pressure and temperature are useful in many fields of applications like technological aspects in the petroleum engineering with the problematic of coal bed methane production, carbon dioxide sequestration or gas shale production [1–10], and computational simulations [11–18]. The main mechanisms of adsorption are known and have been confirmed in the case of ideal fluids near ambient conditions [19–21] but a comprehensive description of the supercritical adsorption on microporous and mesoporous adsorbents is still needed. In this context, the knowledge of the differential enthalpies of adsorption and the adsorption isotherms are of prime importance for a reliable description of the gas–solid interactions at high pressure and temperature. In general, calorimetric methods [21–23] are used for determination of differential enthalpies of adsorption and manometric [24–26] or gravimetric [27, 28] methods for the determination of the amount adsorbed. Direct calorimetric measurements are the most reliable way to determine differential enthalpies of adsorption because they are free from hypotheses from the attainment of equilibrium or on desorption rate law that must be made in indirect determinations [29–41]. Various apparatus have been built to determine simultaneously such quantities [15, 41–53], but some of them operate at low pressures and temperatures range [41–49] others at higher pressures and temperatures close to the ambient conditions [15, 50–53]. Those various recent studies were not made in both high temperature and pressure conditions, because of the difficulty to finalize a complete thermostated coupled apparatus at high temperature. The aim of this study is to determine simultaneously adsorption isotherms and differential enthalpies of adsorption at higher pressures and

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temperatures on microporous and mesoporous materials. In this study, the description of a thermostated combined calorimetric–manometric apparatus is given, this specific experimental device comprising a Setaram C80 differential heat flow calorimeter coupled with a home-built manometric system can work for pressures from vacuum up to 2.5 MPa and temperatures from 303 to 423 K. The reliability of the apparatus and measurements procedures are analyzed and discussed. Both adsorption isotherms and differential enthalpies of adsorption of methane and carbon dioxide have been determined for two microporous-activated carbons.

Experimental

Experimental setup

A specific thermostated experimental device comprising a differential heat flow calorimeter coupled with a manometric system shown in Fig. 1 has been built for this study. The differential heat flow calorimeter is a Tian Calvet Setaram C80 model which measures the heat flux of a gas and can be operated isothermally. The inner part of the calorimeter includes two calorimetric cells; one of those cells was connected to a home-built manometric apparatus design for being inserted in the upper part of the

calorimeter as shown in Fig. 2. The second calorimetric cell is connected to an empty reference cell to stabilize the heat flux. Thanks to the manometric temperature regulation system, the coupled apparatus works under isothermal conditions between 303 and 423 K. The manometric apparatus is made of stainless steel and consist in a set-up with three valves and a pressure transducer P (Fig. 1). All valves are type SS-41GS2-1466 and SS-41GS2-A-1466 from Swagelok. V_c is a calibration cell (1) type SS-4CD-TW-10, provided by Swagelok, which was used for the volume determination of the dosing volume V_d (2) and the volume of the adsorption cell V_{ads} (3), located in one of the two calorimetric cell, in which the porous sample was introduced. The dosing volume V_d is the volume between the valves and the pressure transducer. This volume is used for stocking the adsorptive before sending it in the adsorption cell. The adsorption cell is closed with a 5 μm filter used to avoid the entrainment of little adsorbent particles and to prevent them from settling in the seating of the valves. Thanks to nitrogen expansions from V_c to other part of the apparatus, we have determined the value of the dosing volume V_d and the adsorption cell V_{ads} without sample. The value of V_c has been checked with nitrogen expansions from $(V_{ads} + V_d)$ to V_c at pressures between 0.1 and 0.2 MPa. The calculations were made thanks to the Ideal Gas equation of state; results with accuracy are given in Table 1.

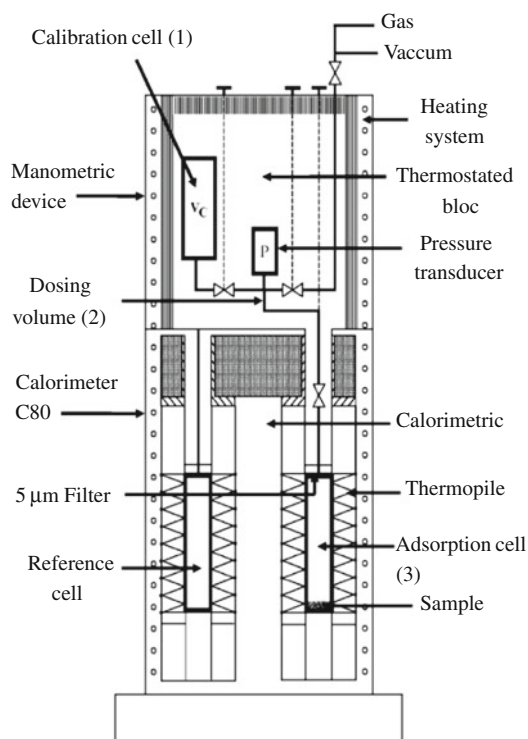


Fig. 1 The thermostated coupled apparatus

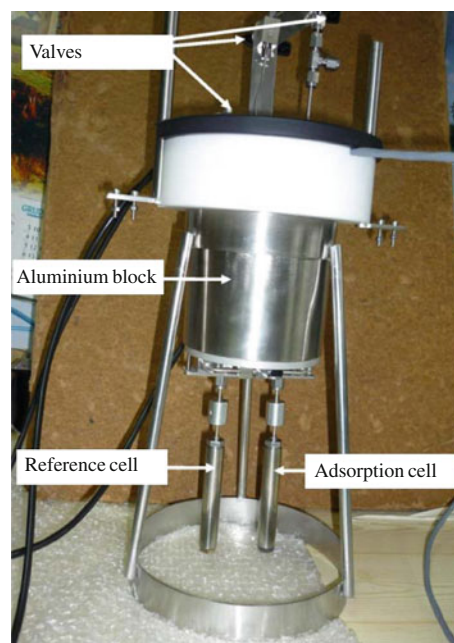


Fig. 2 The manometric apparatus

Table 1 Manometric apparatus volume determination

	V_c	V_d	V_{ads}
Volume/cm ³	9.81	6.30	10.24
Error/%	0.42	0.61	1.18

Pressure measurement

An MKS Baratron type 121A absolute pressure transducer is used for measuring the pressure. With an accuracy of 0.01% of full scale in the range from vacuum to 3.3 MPa, this pressure transducer allows an accurate measurement of the gas phase pressure in contact with the porous sample before and after adsorption. The separate housings of the sensor electronics unit enable the sensor to be heated up to 423 K and allow the electronic units to be mounted in a convenient location.

Manometric apparatus temperature regulation system

The home-made manometric device is plugged into an aluminum block specially designed for being inserted in the upper part of the calorimeter (Fig. 2). At the surroundings of this block, a heating resistor connected to an external PID regulation system is used for heating the manometric system. The same temperature is settled for the calorimeter and the manometric system allowing isothermal conditions in both parts of the coupled apparatus.

Data acquisition system

National instruments data acquisition type PCI-MIO-16XE-50 and LabVIEW program (Fig. 3) are used for measuring the pressure and the calorimetric signals simultaneously. The software used allowed us to watch and

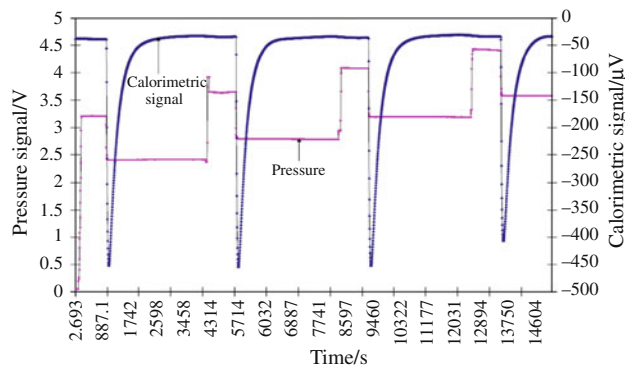


Fig. 4 Pressure and calorimetric signal recorded during an adsorption experiment

record the variation of the calorimetric signals and the pressure drop due to adsorption simultaneously (Fig. 4).

Methods

Carrying out an adsorption measurement (adsorption isotherm and differential enthalpy of adsorption) at one temperature involves several steps:

- (1) Introduce the microporous or mesoporous sample into the adsorption cell and record the initial mass. Depending on the specific surface and the density of the material used for the study, the adsorption cell was filled with an amount of adsorbent sample corresponding at least to a surface of 50 m².
- (2) The adsorbent sample is cleaned by simultaneous evacuation and heating up of the adsorption cell inside the calorimeter during 24 h. The temperature settled depend on the type of adsorbent sample, vacuum was achieved when cleaning the sample.

Fig. 3 LabView software



- (3) An accurate determination of the volume occupied by the adsorbent must be done, this determination is performed using helium expansions from V_d to V_{ads} (filled with the porous sample) at pressures between 0.1 and 0.2 MPa. The resulting dead space depends on the final pressure of helium. This method has the advantage of giving a dead space volume reproducible from an adsorption experiment to another and from a laboratory to another. Helium is used for this determination because it is considered as not adsorbed. Calculations were made thanks to a specific helium equation of state [54].
- (4) The all apparatus is evacuated and the temperature for the study is settled.
- (5) An amount of gas is introduced in V_d . When the equilibrium is reached, pressure and temperature are measured.
- (6) The valve is opened to allow the adsorptive reaching the adsorbent sample in V_{ads} . The gas must be introduced very slowly, so that the heat effect corresponding to the gas compression in the calorimeter may be calculated accurately. This can be done by opening the valve very slowly.
- (7) The calorimetric signal is continuously recorded during the complete step, the equilibrium pressure and temperature are recorded when calorimetric signals returns to baseline.
- (8) The adsorption cell is isolated by closing the valve.
- (9) Steps 5 to 8 are repeated to plot the adsorption isotherm and the differential enthalpies of adsorption.

Determination of the amount adsorbed

The measurements of the total amount of gas n_1 admitted into the volume V_d and the amount of gas n_2 remaining in the gas phase ($V_d + V_{ads}$) at the adsorption equilibrium are determined by p - V - T measurements before and after adsorption (respectively p_1 and p_2) by the use of the Soave-Redlich-Kwong equation of state (Eq. 1).

$$p = \frac{RT}{v-b} - \frac{\frac{a}{\sqrt{T}}}{v(v+b)} \quad (1)$$

It allows calculating the molar volume of the gas before and after adsorption, respectively v_1 and v_2 , by using the experimental conditions in which:

- p is the pressure in Pa
- T is the temperature in K
- v is the molar volume of the adsorptive in $\text{m}^3 \text{mol}^{-1}$
- R is the gas constant in $\text{J mol}^{-1} \text{K}^{-1}$
- The parameter a expresses the relation to the intermolecular interactions:

$$a = \frac{\omega_a R^2 T_c^{2.5}}{p_c} \quad (2)$$

- The parameter b is the co-volume:

$$b = \frac{\omega_b RT_c}{p_c} \quad (3)$$

where

- T_c is the critical temperature of the gas in K,
- p_c is the critical pressure of the gas in Pa.

- ω_a and ω_b are constant values and are function of the acentric factor ω :

$$\omega_a = 0.42137e^{0.27868\omega} \quad (4)$$

$$\omega_b = 0.0855e^{0.29161\omega} \quad (5)$$

The knowledge of the experimental volumes (V_d and V_{ads}), temperatures (T), mass of adsorbent (m) introduced in the adsorption cell and pressures allow deducing, respectively, the molar quantity in the gaseous phase before adsorption n_1 (Eq. 6) and after adsorption n_2 (Eq. 7). It is then possible to calculate the amount adsorbed n_{ads} thanks to Eq. 8.

$$n_1 = \frac{V_d}{v_1} \quad (6)$$

$$n_2 = \frac{V_d + V_{ads}}{v_2} \quad (7)$$

$$n_{ads} = \frac{n_1 - n_2}{m} \quad (8)$$

where V_d is the value of the dosing volume in m^3 , V_{ads} is the volume calculated by helium expansion in m^3 , m is the mass of the microporous or mesoporous sample in g, and n_{ads} is the amount adsorbed in mol g^{-1} .

The errors estimations are about 0.6% on the determination of V_d and about 1.2% on the estimation of V_{ads} . For the molar quantity, the error estimation is about 0.5%, the error on the mass measurement has been considered as negligible, which lead to an error of 3.6% on the determination of n_{ads} . The data presented in this study are Gibbs (or excess) adsorption [21].

Determination of the differential enthalpy of adsorption

Each introduction of gas in the adsorption cell is followed by an exothermal effect until equilibrium is reached. In this procedure, one must consider that the gas is introduced reversibly. The calorimetric adsorption cell is then considered as an open system and the calorimetric signal E (expressed in μV) recorded by the thermopiles provides the total heat Q_g resulting from two contributions: the heat of adsorption Q_{ads} and the heat dissipated by the compressed gas Q_{comp} :

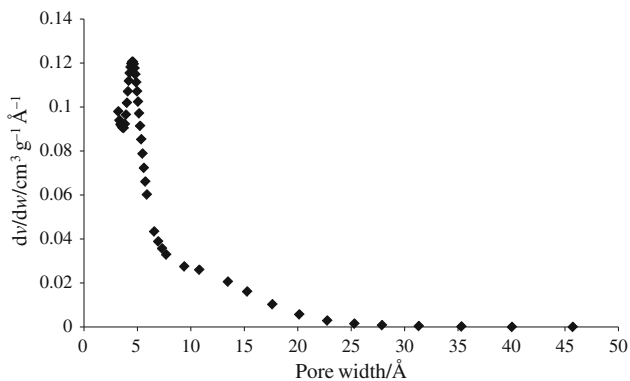


Fig. 5 EcoSorb-activated carbon Pore Size Distribution Function

Table 2 Properties of microporous adsorbent

	Specific BET surface area/m ² g ⁻¹	Micropores volume/cm ³ g ⁻¹
F400	1063	0.51
EcoSorb	1290	0.6

Table 3 Critical properties and acentric factors of the adsorptive

Adsorptive	CO ₂	CH ₄
T _c /K	304.128	190.654
P _c /MPa	7.3773	4.5992
ω	0.2239	0.0114

$$Q_g = Q_{ads} + Q_{comp} \tag{9}$$

where

$$Q_g = k \int E(t) dt \tag{10}$$

Q_g is the total heat measured by the thermopiles in J, Q_{ads} is the adsorption heat in J, Q_{comp} is the heat dissipated by the compressed gas in J, E(t) is the calorimetric signal recorded in μV, k is the static gain of the calorimetric detector in W (μV)⁻¹ previously measured [55].

The determination of Q_{comp} can be done thanks to the following Maxwell equation:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\alpha_p V \tag{11}$$

where α_p is the isobaric expansion coefficient defined by 1/V (∂V/∂T)_p. In a mass-open type calorimeter vessel (used in this study), the quantity of heat δQ_{comp} dissipated by the pressure drop dp under isothermal conditions is a sum of two opposite effects: one resulting from the gas and the other from the vessel wall [56]:

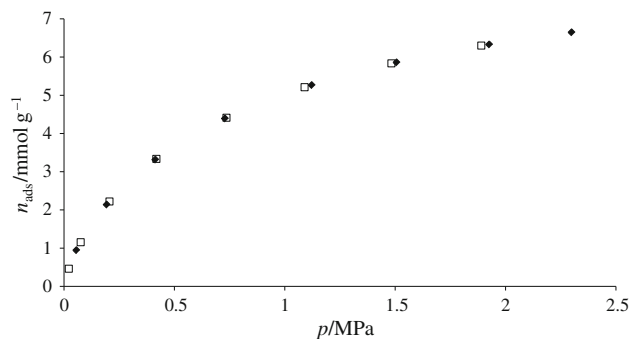


Fig. 6 CO₂ adsorption isotherm on F400-activated carbon at 318 K. Reproducibility test (filled diamonds) Run 1; (open squares) Run 2

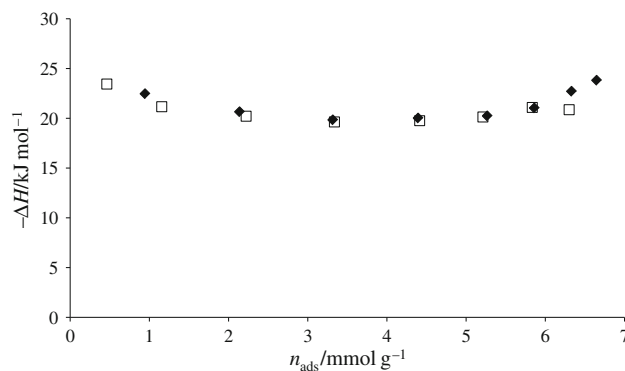


Fig. 7 CO₂ differential enthalpies of adsorption on F400-activated carbon at 318 K. Reproducibility test (filled diamonds) Run 1; (open squares) Run 2

Table 4 CO₂ adsorption isotherms data on Filtrasorb F400-activated carbon at 318 K

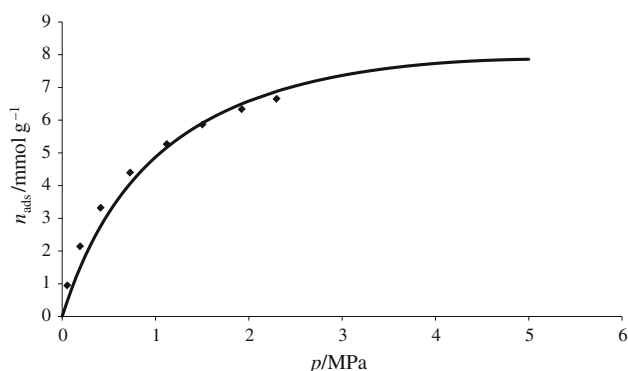
Filtrasorb F400			
CO ₂			
Run 1		Run 2	
p/MPa	n _{ads} /mmol g ⁻¹	p/MPa	n _{ads} /mmol g ⁻¹
0.06	0.946	0.02	0.463
0.19	2.139	0.08	1.157
0.41	3.317	0.21	2.222
0.73	4.393	0.42	3.337
1.12	5.267	0.74	4.413
1.51	5.861	1.09	5.212
1.93	6.331	1.48	5.835
2.30	6.648	1.89	6.300

$$\delta Q_{comp} = \alpha_{ss} V_E T dp - \alpha_p V_E T dp \tag{12}$$

where α_{ss} is the isobaric coefficient of stainless steel in K⁻¹ (the material of which the adsorption cell is made), T the temperature in K, and V_E is the volume taken into account by the thermopiles deduced by helium measurement in m³.

Table 5 CO₂ differential enthalpies of adsorption data on Filtrasorb F400-activated carbon at 318 K

Filtrasorb F400			
CO ₂			
Run 1		Run 2	
$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$	$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$
0.946	22.5	0.463	23.4
2.139	20.7	1.157	21.2
3.317	19.8	2.222	20.2
4.393	20.0	3.337	19.6
5.267	20.2	4.413	19.8
5.861	21.0	5.212	20.1
6.331	22.7	5.835	21.1
6.648	23.8	6.300	20.9

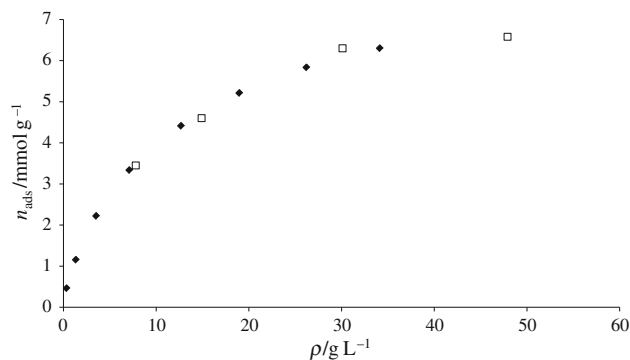
**Fig. 8** F400 adsorption isotherm comparison with FP Mons results (filled diamonds) Run 1; (thick line) FP Mons

As small pressure steps Δp are applied in this study, the heat dissipated by the compressed gas can be expressed in the following form:

$$Q_{\text{comp}} = -V_E(\alpha_P - \alpha_{\text{ss}})T\Delta p \quad (13)$$

Thanks to Eq. 13 it is then possible to calculate a corrective term for the compression of the gas and the deformation of the cell which is the novelty in the new of determining the differential enthalpies of adsorption.

The volume taken into account by the thermopiles V_E can be deduced thanks to helium expansions from the dosing volume to the adsorption cell filled with the adsorbent. Helium is considered as not adsorbed, as a consequence the calorimetric signal recorded is only due to the heat dissipated by the compressed gas into the adsorption cell. By the knowledge of the helium isobaric coefficient $\alpha_{P\text{He}}$ and by calculating the integral of the calorimetric signal, it is possible to calculate V_E thanks to Eq. 14:

**Fig. 9** F400 adsorption isotherm comparison with Zurich (filled diamonds) Run 1; (open squares) ETH Zurich

$$V_E = \frac{k \int E(t)dt}{-(\alpha_{P\text{He}} - \alpha_{\text{ss}})T\Delta p} \quad (14)$$

by combining Eqs. 9 to 14 the differential enthalpy of adsorption can be deduced thanks to Eq. 15:

$$\Delta H = \frac{Q_{\text{ads}}}{\Delta n} = \frac{k \int E(t)dt + V_E(\alpha_P - \alpha_{\text{ss}})T\Delta p}{\Delta n} \quad (15)$$

where ΔH is the differential enthalpy of adsorption in J mol^{-1} , Δn is the amount of gas adsorbed between each step of the experiment in mol, Δp is the pressure drop during adsorption experiments in Pa.

The procedure used to determine V_E leads to an uncertainty of 2% on Q_{comp} . The error associated to the total heat Q_g estimated by a test of reproducibility is about 1%. The error in the determination of Q_{ads} results from two additive causes of error in the successive determinations of Q_g and Q_{comp} . Combining errors on both Q_{ads} and n_{ads} , the error on the differential enthalpy of adsorption ΔH is 4%.

Materials

Commercially available Filtrasorb F400 from Chemviron Carbon and EcoSorb-activated carbon from Jacobi carbons were used as microporous adsorbent material. Filtrasorb F400-activated carbon is a well characterized material which is considered as a benchmark material and has been used in many previous studies [57–60]. The EcoSorb-activated carbon was characterized with a Micromeritics ASAP 2020 System. The pore size distribution was determined by a low pressure nitrogen adsorption isotherm at 77 K (from 5×10^{-7} to 0.99 p/p_0 in relative pressure range) evaluated by the Horvath and Kawazoe model [61]. The Pore Size Distribution Function given in Fig. 5 shows that the peak pore diameter is about 4.6 Å. The properties of these microporous adsorbent are given in Table 2. The adsorptive gases used were methane (CH₄) and

Table 6 CH₄ adsorption isotherms data on EcoSorb-activated carbon

EcoSorb-activated carbon					
CH ₄					
T = 323 K		T = 353 K		T = 383 K	
p/MPa	n _{ads} /mmol g ⁻¹	p/MPa	n _{ads} /mmol g ⁻¹	p/MPa	n _{ads} /mmol g ⁻¹
0.02	0.136	0.05	0.177	0.06	0.116
0.06	0.296	0.19	0.516	0.13	0.242
0.11	0.481	0.35	0.825	0.23	0.386
0.17	0.689	0.54	1.127	0.45	0.691
0.25	0.914	0.73	1.391	0.61	0.870
0.35	1.145	0.95	1.649	0.78	1.045
0.45	1.364	1.17	1.862	0.95	1.199
0.56	1.544	1.47	2.125	1.16	1.357
0.67	1.715	1.72	2.314	1.36	1.508
0.78	1.872	2.00	2.512	1.55	1.638
0.90	2.041	2.24	2.657	1.80	1.794
1.04	2.201			2.03	1.929
1.16	2.355				
1.31	2.502				
1.47	2.673				
1.68	2.853				
1.86	3.016				

Table 7 CO₂ adsorption isotherms data on EcoSorb-activated carbon

EcoSorb-activated carbon					
CO ₂					
T = 323 K		T = 353 K		T = 383 K	
p/MPa	n _{ads} /mmol g ⁻¹	p/MPa	n _{ads} /mmol g ⁻¹	p/MPa	n _{ads} /mmol g ⁻¹
0.03	0.302	0.04	0.280	0.06	0.207
0.08	0.794	0.11	0.632	0.14	0.464
0.17	1.421	0.22	1.036	0.27	0.783
0.30	2.100	0.36	1.498	0.40	1.075
0.46	2.716	0.52	1.940	0.55	1.364
0.63	3.335	0.68	2.328	0.71	1.641
0.83	3.899	0.86	2.699	0.88	1.901
1.01	4.347	1.04	3.021	1.06	2.159
1.19	4.743	1.23	3.339	1.23	2.381
1.38	5.094	1.41	3.608	1.41	2.591
1.56	5.402	1.61	3.874	1.58	2.780
1.74	5.674	1.76	4.070	1.75	2.955
1.92	5.929	1.93	4.253	1.92	3.120
2.09	6.161	2.12	4.450	2.10	3.282

carbon dioxide (CO₂) with 99.9% purity. The properties of CH₄ and CO₂ are given in Table 3.

Results and discussions

Reliability

For checking the good operating of our coupled apparatus, we made CO₂ adsorption isotherms measurements at 318 K on the F400-activated carbon which is considered as a benchmark. We made comparison with the results obtain by an inter-laboratory study [59] conducted among four European research laboratories and those obtain by the Zurich Institute of Process Engineering [58]. In those studies, the measurements on Filtrasorb F400 were made at 318 K up to 16 MPa. The CO₂ adsorption isotherms results obtain in the inter-laboratory study were given by an empirical equation, with the appropriate correlated parameters, no experimental results were given. The Zurich Institute of Process Engineering study presents the experimental excess adsorption results versus the carbon dioxide density ρ. We choose to make comparison with both studies because the first one gives parametrical results and the second one directs experimental results. The comparison with the empirical equation results will give us a first

idea of the validity of our results and the comparison with the experimental measurements will show us if our results are reliable. A mass of 0.945 g of F400-activated carbon was degassed at 473 K during 24 h before being used in the adsorption measurement. Two independent sets of measurement (Run 1 and Run 2) were performed; the average deviation is less than 0.5 and 2.5% for adsorption isotherms and differential adsorption enthalpies, respectively. The F400 sample has been outgases at 473 K during 24 h between the two sets of measurements. The results are shown in Fig. 6 for the adsorption isotherms and Fig. 7 for the differential enthalpies of adsorption. Tables 4 and 5 give the experimental data of the adsorption isotherms and differential enthalpies of adsorption, respectively. We can notice that there is no effect of accumulation which shows that the outgassing made for this study is supposed to be enough to empty the micropores. Figure 8 shows the comparison of our experimental data for CO₂ with the results obtains by FP Mons laboratory from the European inter-laboratory study. We chose to compare our measurements with the FP Mons results because their cleaning protocol and their adsorbent sample mass were close of our. At low pressures (p < 0.5 MPa) the average deviation is about 36%, when p > 0.5 MPa the average deviation is about 6.3%. Those deviations can be explained by the fact that the parameters of the empirical equation have been calculated between 0 and 16 MPa, as a consequence the points calculated at low (P < 0.5 MPa) are not representative. We can see that for pressures higher than 0.5 MPa,

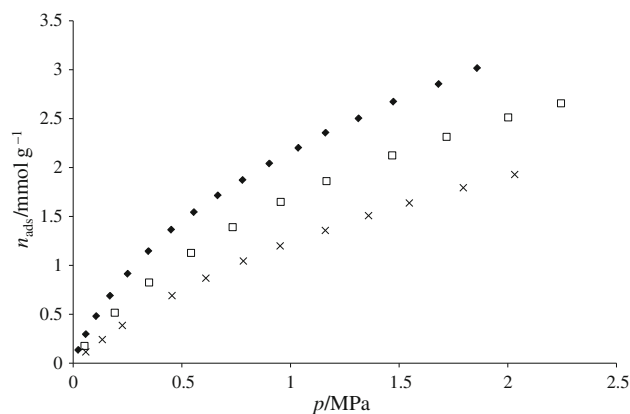


Fig. 10 CH₄ adsorption isotherms on EcoSorb-activated carbon (filled diamonds) 323 K; (open squares) 353 K; (times) 383 K

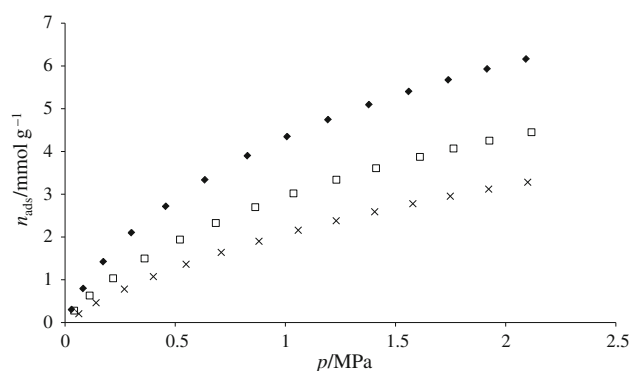


Fig. 11 CO₂ adsorption isotherms on EcoSorb-activated carbon (filled diamonds) 323 K; (open squares) 353 K; (times) 383 K

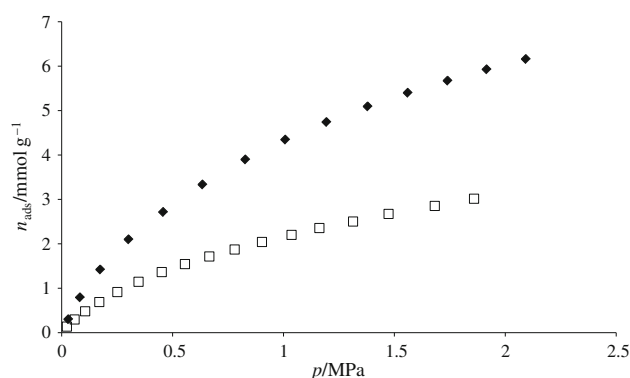


Fig. 12 CO₂ and CH₄ adsorption isotherm comparison at 323 K (filled diamonds) CO₂; (open squares) CH₄

the comparison between the results obtained can be considered as good. Furthermore, Fig. 8 shows us good agreement between the two curves. Figure 9 presents the comparison of our experimental data with those obtained by Zurich Institute of Process Engineering study. This comparison reveals good agreement between the data, in

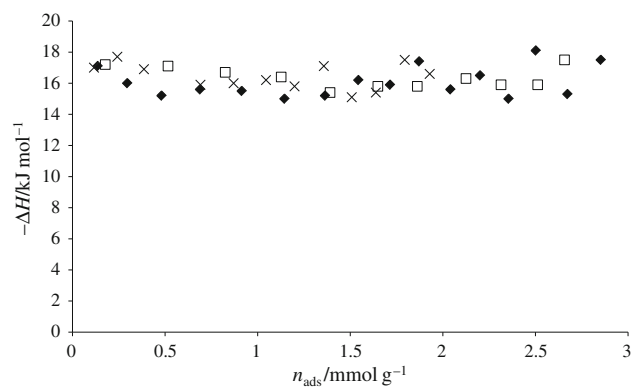


Fig. 13 CH₄ differential enthalpies of adsorption on EcoSorb-activated carbon (filled diamonds) 323 K; (open squares) 353 K; (times) 383 K

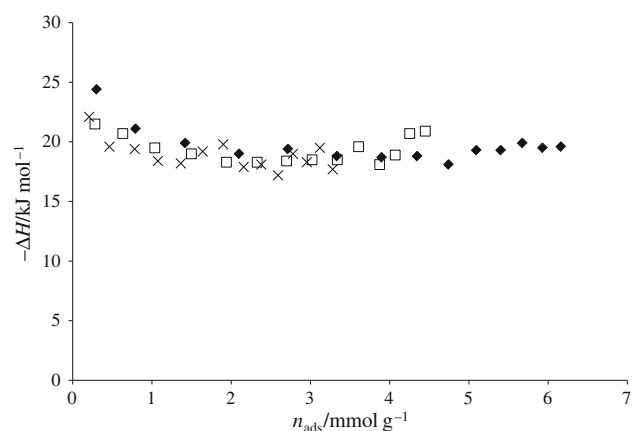


Fig. 14 CO₂ differential enthalpies of adsorption on EcoSorb-activated carbon (filled diamonds) 323 K; (open squares) 353 K; (times) 383 K

fact, the average deviation is less than 3%, which confirm the good operating of our coupled apparatus. The adsorption isotherm highlights a type I isotherm expected in the case of micropores filling. The differential enthalpies of adsorption are constant and close to 21.1 kJ mol⁻¹, this constant value is the result of the interaction between the adsorptive and a homogeneous energetic adsorbent.

Methane and carbon dioxide adsorption on EcoSorb-activated carbon

Adsorption experiments were performed along three isotherms (323, 353, and 383 K) for pressures ranging from vacuum to 2.5 MPa. A mass of 1.0237 g of EcoSorb-activated carbon has been degassed at 423 K during 24 h before the experiments. The experimental data for methane and carbon dioxide are listed in Tables 6 and 7. Figures 10 and 11 present the adsorption isotherms of CH₄ and CO₂ on EcoSorb-activated carbon. Both methane and carbon

Table 8 CH₄ differential enthalpies of adsorption data on EcoSorb-activated carbon

EcoSorb					
CH ₄					
T = 323 K		T = 353 K		T = 383 K	
$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$	$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$	$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$
0.136	17.1	0.177	17.2	0.116	17
0.296	16	0.516	17.1	0.242	17.7
0.481	15.2	0.825	16.7	0.386	16.9
0.689	15.6	1.127	16.4	0.691	15.9
0.914	15.5	1.391	15.4	0.87	16
1.145	15	1.649	15.8	1.045	16.2
1.364	15.2	1.862	15.8	1.199	15.8
1.544	16.2	2.125	16.3	1.357	17.1
1.715	15.9	2.314	15.9	1.508	15.1
1.872	17.4	2.512	15.9	1.638	15.4
2.041	15.6	2.657	17.5	1.794	17.5
2.201	16.5			1.929	16.6
2.355	15				
2.502	18.1				
2.673	15.3				
2.853	17.5				

Table 9 CO₂ differential enthalpies of adsorption data on EcoSorb-activated carbon

EcoSorb					
CO ₂					
T = 323 K		T = 353 K		T = 383 K	
$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$	$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$	$n_{\text{ads}}/\text{mmol g}^{-1}$	$-\Delta H/\text{kJ mol}^{-1}$
0.302	24.4	0.28	21.5	0.207	22.1
0.794	21.1	0.632	20.7	0.464	19.6
1.421	19.9	1.036	19.5	0.783	19.4
2.1	19	1.498	19	1.075	18.4
2.716	19.4	1.94	18.3	1.364	18.2
3.335	18.8	2.328	18.3	1.641	19.2
3.899	18.7	2.699	18.4	1.901	19.8
4.347	18.8	3.021	18.5	2.159	17.9
4.743	18.1	3.339	18.5	2.381	18.1
5.094	19.3	3.608	19.6	2.591	17.2
5.402	19.3	3.874	18.1	2.78	19
5.674	19.9	4.07	18.9	2.955	18.3
5.929	19.5	4.253	20.7	3.12	19.5
6.161	19.6	4.45	20.9	3.282	17.7

dioxide exhibit an expected type I behavior among the IUPAC classification but at the highest pressure studied, the saturation of the adsorbent is not reached. Furthermore, the adsorption of CO₂ is about twice as important as in methane (Fig. 12). The differential enthalpies of adsorption

are shown in Fig. 13 for CH₄ adsorption and in Fig. 14 for CO₂ adsorption, the data are reported in Tables 8 and 9. The differential enthalpies of adsorption were plotted versus the amount adsorbed for each isotherm. These isotherms plots exhibit that the differential enthalpies of

adsorption do not vary between 323 and 383 K, which reveals that the porous adsorbents studied are homogeneous. The comparisons between the results obtained show that the differential enthalpy of adsorption increases when the adsorption capacities are better for a given adsorbent. Thus, the differential enthalpies of adsorption are 19.3 kJ mol^{-1} for carbon dioxide and 16.3 kJ mol^{-1} for methane on EcoSorb-activated carbon. It is relevant to note that these values, which should be analyzed as competitive effect between adsorbent-adsorptive and adsorptive-adsorptive interactions, are not affected by the temperature in the extended range investigated. This original information obtained on a well-characterized carbon can be used as a discriminatory test for the appropriate interaction potential choice to make in supercritical conditions molecular simulations, as the molecular parameters involved in the intermolecular potential are generally adjusted close to standards conditions.

Conclusions and perspectives

A new thermostated coupled apparatus have been built. This new apparatus can measure simultaneously adsorption isotherms and differential enthalpies of adsorption for pressures from vacuum up to 2.5 MPa and temperatures from 303 to 423 K. After establishing the reliability of the thermostated coupled apparatus, methane and carbon dioxide adsorption isotherms and enthalpies of adsorption have been determinate on EcoSorb-activated carbon between 323 and 383 K. This study is the first stage of a study consisting in determining in a complete way the physical properties of microporous and mesoporous adsorbents at high pressure and high temperature. A second stage would consist in studying the adsorption on a mesoporous adsorbent and studying the simulation of the adsorption phenomenon at high pressure and high temperature thanks to appropriate interaction potential determined by experimental measurements.

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